



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 855 366 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
29.07.1998 Bulletin 1998/31

(51) Int. Cl.⁶: C01B 3/38

(21) Application number: 98100669.5

(22) Date of filing: 16.01.1998

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 22.01.1997 US 35396 P

(71) Applicant: Haldor Topsoe A/S
DK-2800 Lyngby (DK)

(72) Inventors:
• Rostrup-Nielsen, Jens
2830 Virum (DK)
• Christensen, Peter Seier
2400 Copenhagen NV (DK)
• Hansen, Viggo Lucassen
2700 Bronshøj (DK)

(54) **Synthesis gas production by steam reforming using catalyzed hardware**

(57) Process for the preparation of hydrogen of carbon monoxide rich gas by steam reforming of a hydrocarbon feedstock in presence of a steam reforming catalyst supported as thin film on a tubular reactor, comprising steps of

(a) optionally passing a process gas of prereformed hydrocarbon feedstock through a first tubular reactor with a thin film of steam reforming catalyst supported on walls of the reactor in heat conducting relationship with hot flue gas from a subsequent second tubular steam reforming reactor;

(b) passing effluent from the first tubular reactor to the subsequent second tubular reactor being provided with a thin film of the steam reforming catalyst and being heated by burning of fuel, thereby obtaining a partially steam reformed gas effluent and the hot flue gas;

(c) passing the effluent from the second reactor to a fixed bed steam reforming catalyst; and

(d) withdrawing from the fixed bed a product gas of the hydrogen and carbon monoxide rich gas.

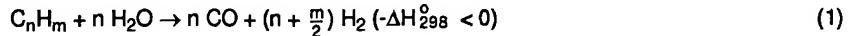
EP 0 855 366 A1

Description

The present invention is directed to the production of synthesis gas by steam reforming of a hydrocarbon feedstock in contact with catalyzed hardware.

5 The term catalyzed hardware is used for a catalyst system where a layer of catalyst is fixed on a surface of another material, e.g. metallic surfaces. The other material serves as the supporting structure giving strength to the system. This allows to design catalyst shapes which would not have sufficient mechanical strength in itself. The system herein consists of tubes on which a thin layer of reforming catalyst is placed on the inner wall.

Synthesis gas is produced from hydrocarbons by steam reforming by the reactions (1)-(3):



State of the art steam reforming technology makes use of reforming catalyst in the form of pellets of various sizes and shapes. The catalyst pellets are placed in fixed bed reactors (reformer tubes). The reforming reaction is endothermic. In conventional reformers, the necessary heat for the reaction is supplied from the environment outside the tubes 20 usually by a combination of radiation and convection to the outer side of the reformer tube. The heat is transferred to the inner side of the tube by heat conduction through the tube wall, and is transferred to the gas phase by convection. Finally, the heat is transferred from the gas phase to the catalyst pellet by convection. The catalyst temperature can be more than 100°C lower than the inner tube wall temperature at the same axial position of the reformer tube.

It has been found that heat transport is more efficient when catalyzed hardware is used in the steam reforming 25 process. The heat transport to the catalyst occurs by conduction from the inner tube wall. This is a much more efficient transport mechanism than the transport by convection via the gas phase. The result is that the temperatures of the inner tube wall and the catalyst are almost identical (the difference below 5°C) Furthermore, the tube thickness can be reduced, see below, which makes the temperature difference between the inner and outer side of the reformer tube 30 smaller. It is hence possible to have both a higher catalyst temperature and a lower tube temperature, all other conditions being the same when replacing the conventional reformer tubes with catalyzed hardware tubes. A low outer tube wall temperature is desirable since it prolongs the lifetime of the tube. A high catalyst temperature is advantageous since the reaction rate increases with temperature and since the equilibrium of reaction (3) is shifted to the right hand side resulting in a better utilisation of the feed.

Accordingly, this invention provides a process for the preparation of hydrogen of carbon monoxide rich gas by 35 steam reforming of a hydrocarbon feedstock in presence of a steam reforming catalyst supported as thin film on a tubular reactor, comprising steps of:

- (a) optionally passing a process gas of prereformed hydrocarbon feedstock through a first tubular reactor with a thin 40 film of steam reforming catalyst supported on walls of the reactor in heat conducting relationship with hot flue gas from a subsequent second tubular steam reforming reactor;
- (b) passing effluent from the first tubular reactor to the subsequent second tubular reactor being provided with a thin film of the steam reforming catalyst and being heated by burning of fuel, thereby obtaining a partially steam reformed gas effluent and the hot flue gas;
- (c) passing the effluent from the second reactor to a fixed bed steam reforming catalyst; and
- 45 (d) withdrawing from the fixed bed a product gas of the hydrogen and carbon monoxide rich gas.

Pressure drop in the catalyzed reformer tube is much lower than in the conventional case for the same tube diameter. This enables the use of reactor tubes with a smaller diameter and still maintaining an acceptable pressure drop. Smaller tube diameter results in an increased tube lifetime, tolerates higher temperatures and reduces the tube material 50 consumption.

Finally, the catalyst amount is reduced when using catalyzed hardware reformer tubes compared to the conventional reformer with a fixed bed of reforming catalyst.

Fig. 1 shows the front-end of a plant producing syngas. Feed 2 is preheated, desulphurized in unit 4, mixed with process steam 6, and further heated before entering an adiabatic prereformer 8. The effluent stream from prereformer 55 8 is further heated in loop arranged in flue gas channel 12 and send to the tubular reformer 14, where conversion of methane to hydrogen, carbon monoxide, and carbon dioxide occurs. The processing of effluent gas downstream from the tubular reformer depends on the use of the product.

Catalyzed hardware can be used in two of the units shown in Fig. 1:

1. In the preheater coil 10 for heating the prereformer effluent gas before entering the tubular reformer 14.
2. In the tubular reformer 14.

Below is presented the results obtained for the plant in Fig. 1 when catalyzed hardware is used in the above two units. The catalyst used for the catalyzed hardware is the R-67R nickel steam reforming catalyst available from Haldor Topsoe A/S. The results are compared with the conventional case.

The purpose of the preheater coil is to use the heat content in the flue gas for preheating of the process gas before it enters the tubular reformer. The flue gas is used for preheating of process gas and for preheating of the combustion air for the tubular reformer (not shown in Fig. 1). However, the heat content of the flue gas is larger than what can be used for these purposes and the remaining heat is used for steam production. It will be an advantage, if a larger amount of the heat content in the flue gas can be transferred to the process gas. This will reduce the necessary amount of fuel in the tubular reformer, and it will reduce the size of the reformer since a smaller amount of heat is to be transferred in the unit.

The conventional preheater is limited by the risk of carbon formation by decomposition of methane. This sets an upper limit for the tube wall temperature, which can be accepted. Fixing a layer of catalyzed hardware on the inner tube wall 6 of the preheater coil 10 (as shown in Fig. 2) results in a decrease of both the tube wall temperature and the process gas temperature. This enables the transfer of a higher duty in the coil without having a higher tube temperature.

The preheater coil used in the calculation consists of 8 tubes in which the process gas flow inside the tubes. The flue gas flows on the outer side. The flow pattern is cross flow/co-current. Fig. 2 shows the layout for one tube. The two cases with and without catalyzed hardware are summarised in Table 1. It is apparent that the transferred duty (heat energy) is 49% higher in the catalyzed hardware case compared to the conventional case. The catalyst layer thickness in the catalyst hardware case is 1.0 mm.

Table 1

	Conventional case	Catalyzed hardware case
Number of tubes	8	8
Total effective tube length	51.6 m	76.2 m
Flue gas in/out temperature	1057°C/964°C	1057°C/912°C
Process gas in/out temperature	512°C/650°C	512°C/631°C
Methane conversion	0%	8.7%
Transferred duty	$9.69 \cdot 10^6$ kcal/h	$1.44 \cdot 10^7$ kcal/h

The effective tube length is the length of the tube inside the flue gas channel.

The conventional tubular reformer consists of a number of tubes which is filled with catalyst pellets. The process gas flows inside the tubes. The tubes are placed in a furnace which is heated by combustion of a fuel.

In the catalyzed hardware case the catalyst pellet filled tubes are replaced with a number of tubes with a layer of catalyzed hardware on the inner tube wall. The catalyst layer thickness is 0.25 mm. An additional adiabatic reforming fixed bed reactor is placed downstream from the tubular reactor since the conversion of methane in the catalyzed hardware tubular reformer is inferior to the conventional case. This reactor is called post reformer. The catalyst used in the post reformer is the RKS-2 nickel steam reforming catalyst available from Haldor Topsoe A/S.

The two cases are summarised below in Table 2. It is seen that catalyst consumption is decreased by a factor 11.5, and that material consumption for the tubes in the tubular reformer is decreased 24% in the catalyzed hardware case compared to the conventional case.

Table 2

	Conventional case	Catalyzed hardware reformer	Catalyzed hardware case + post reformer
Number of tubes	276	187	
Tube length	13 m	55 m	

Table 2 (continued)

	Conventional case	Catalyzed hardware reformer	Catalyzed hardware case + post reformer
Catalyst consumption	31.0 t	0.63 t	2.70 t
Tube material consumption for tubular reformer	153.6 t	116.0 t	
Methane conversion	89.0 %	80.7 %	90.2 %

5 A flow scheme of a process according to the invention is shown in Fig. 3. The numbers in the triangles refer to the table below in which the overall figures for the process are compared. The fuel consumption is decreased by 7.4% in the catalyzed hardware case compared to the conventional case.

10

15

20

25

30

35

40

45

50

55

Table 3

Position		Conventional case	Catalysed hardware case
1	T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄	512 28.5 57851 143168 23.78 0.74 21.14 54.34	512 28.5 57851 143168 23.78 0.74 21.14 54.34
2	T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄	650 27.5 57851 143168 23.78 0.74 21.14 54.34	631 27.4 67397 148720 34.58 2.67 20.16 42.59
3	T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄	925 24.1 141533 199121 68.85 20.24 8.47 2.44	1015 26.0 132653 194106 66.76 20.42 8.24 4.57
4	T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄	No post reformer in this case	930 24.4 142580 200003 69.08 20.35 8.40 2.17
5	T (°C) Total flow (Nm ³ /h)	1057 244672	1057 234677
6	T (°C)	964	912
7	Total flow (Nm ³ /h)	9524	8820

55

Claims

1. Process for the preparation of hydrogen or carbon monoxide rich gas by steam reforming of a hydrocarbon feed-

stock in presence of a steam reforming catalyst supported as thin film on a tubular reactor, comprising steps of

5 (a) optionally passing a process gas of prereformed hydrocarbon feedstock through a first tubular reactor with
a thin film of steam reforming catalyst supported on walls of the reactor in heat conducting relationship with hot
flue gas from a subsequent second tubular steam reforming reactor;

10 (b) passing effluent from the first tubular reactor to the subsequent second tubular reactor being provided with
a thin film of the steam reforming catalyst and being heated by burning of fuel, thereby obtaining a partially
steam reformed gas effluent and the hot flue gas;

15 (c) passing the effluent from the second reactor to a fixed bed steam reforming catalyst; and

(d) withdrawing from the fixed bed a product gas of the hydrogen and carbon monoxide rich gas.

20 2. Process of claim 1, wherein the fixed bed steam reforming catalyst is operated at adiabatic condition.

3. Process of claim 1, wherein the fixed bed steam reforming catalyst is arranged within the second tubular reactor.

4. Process of claim 1, wherein the steam reforming catalyst comprises nickel and/or ruthenium.

25

30

35

40

45

50

55

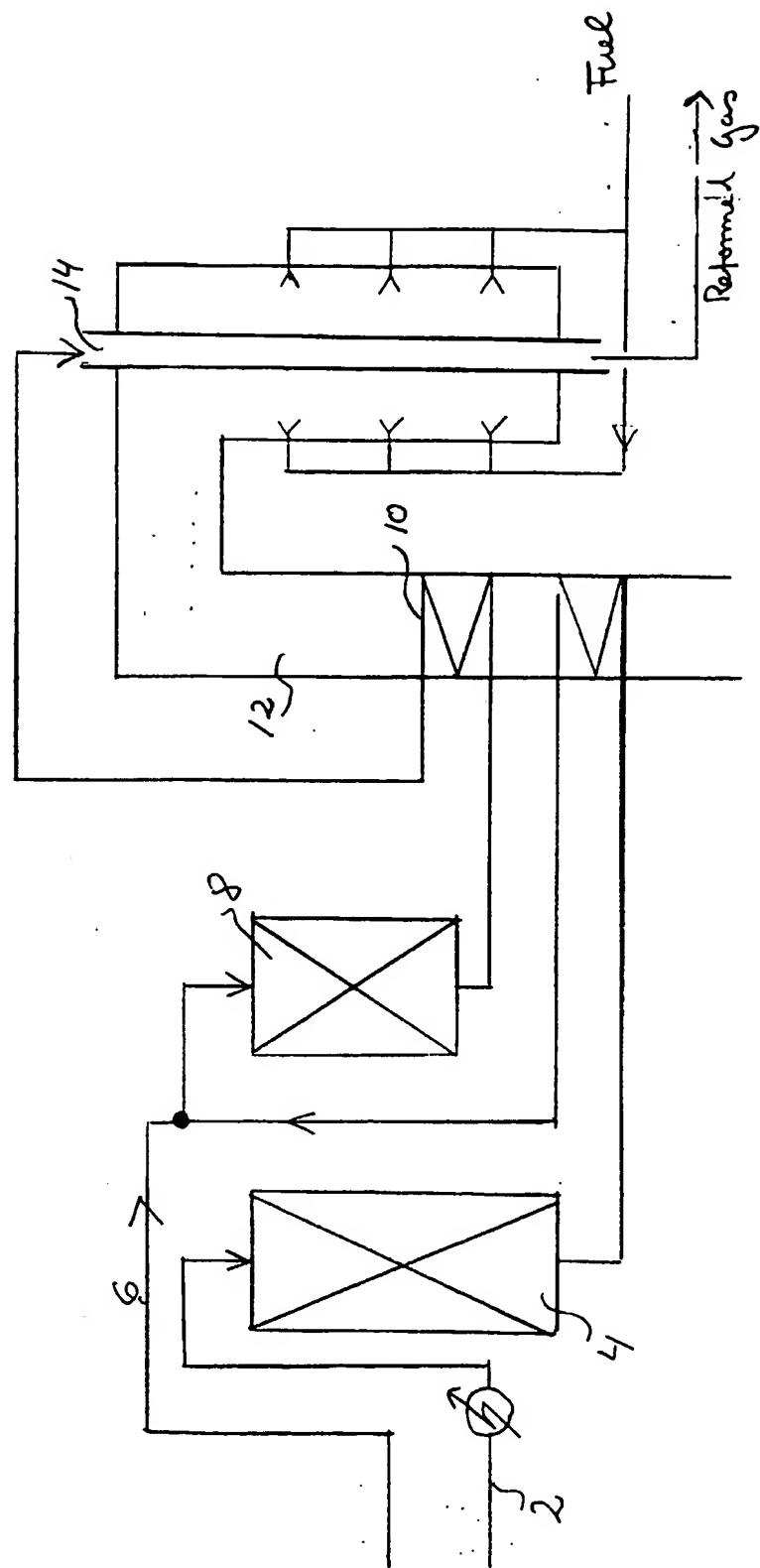


FIG. 1

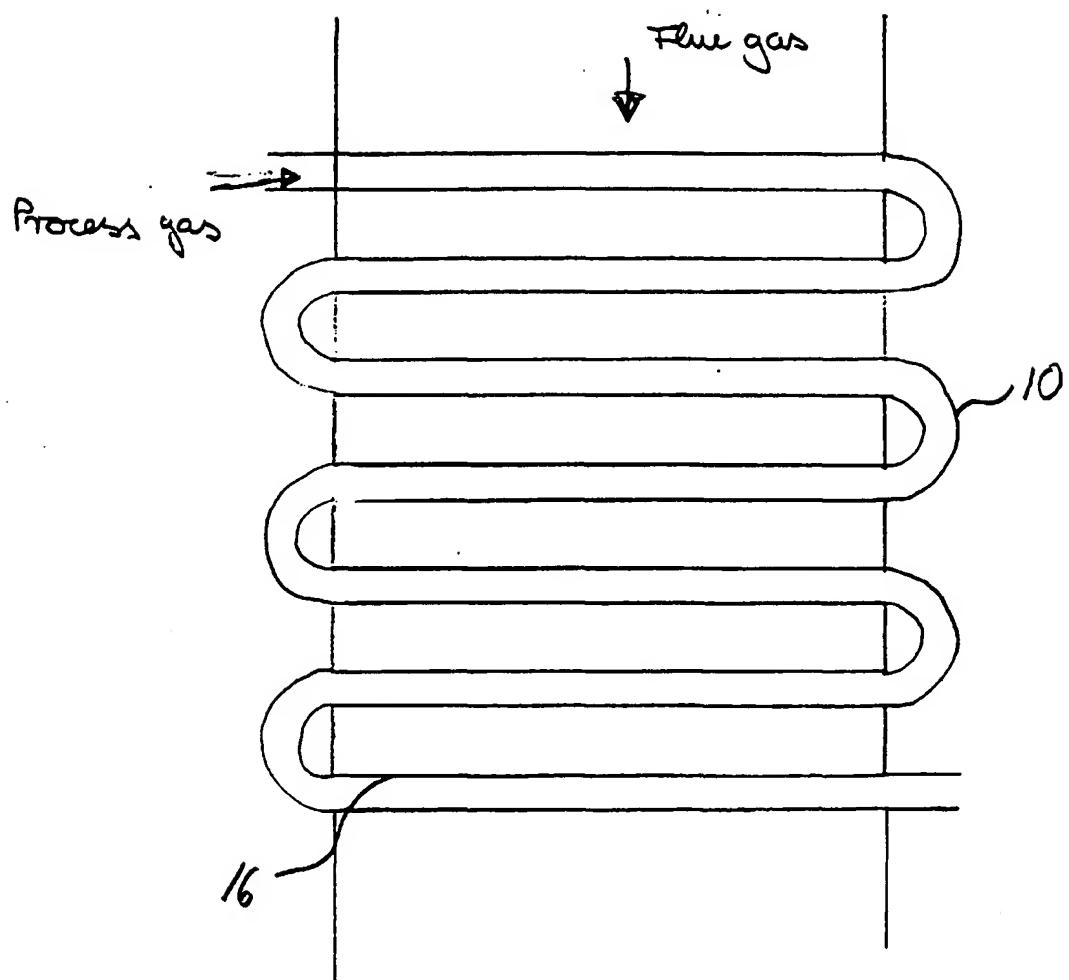


FIG. 2

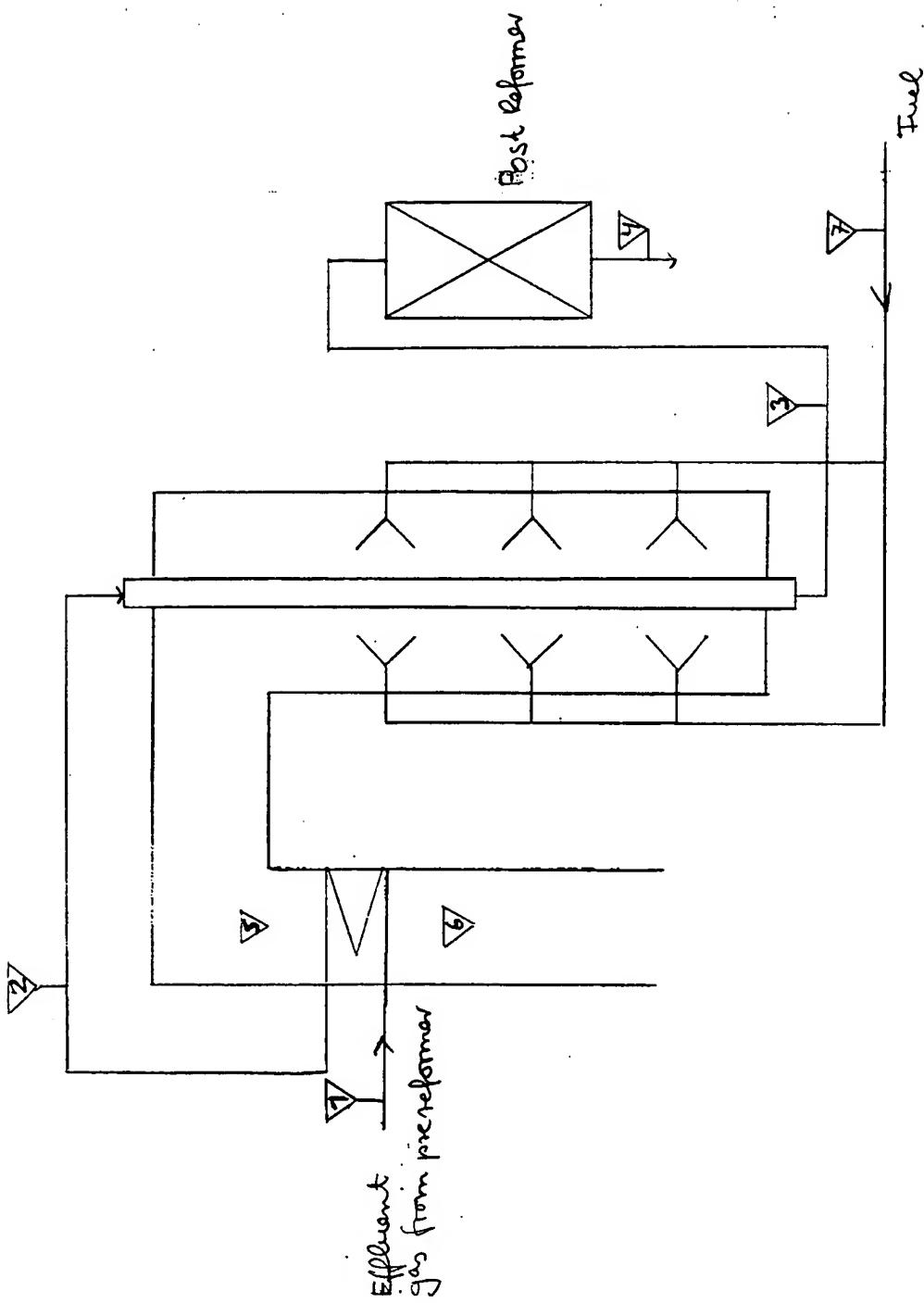


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 0669

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	EP 0 124 226 A (ICI PLC) * page 2, line 3 - page 4, line 30; claim 8 *	1	C01B3/38
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 551 (C-1117), 5 October 1993 & JP 05 155602 A (SEKIYU SANGYO KASSEIKA CENTER; OTHERS: 01), 22 June 1993, * abstract *	1	
A	US 4 400 309 A (MCMAHON JOSEPH F ET AL) * column 1, line 17 - line 53 *	1	
A	EP 0 440 258 A (TOPSOE HALDOR AS) * page 5, line 36 - page 6, line 1 *	1	
A	EP 0 437 059 A (ICI PLC) * claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C01B
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
BERLIN	11 May 1998	Clement, J-P	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			